

(12) UK Patent Application (19) GB (11) 2 316 021 (13) A

(43) Date of A Publication 18.02.1998

(21) Application No 9716893.4	(51) INT CL ⁶ C03C 17/06
(22) Date of Filing 08.08.1997	
(30) Priority Data (31) 9616735 (32) 09.08.1996 (33) GB	(52) UK CL (Edition P) B2E EAH E1106 E1201 E1536 E1701 E1743 E407T E507S E611T C7F FPEL FR841 FR871 FR872 FR911 F782 U1S S1134 S1820 S1825 S2286 S3037
(71) Applicant(s) Trip Productions B.V. (Incorporated in the Netherlands) Vennestraat 11, 2161 LE LISSE, Netherlands	(56) Documents Cited US 3971692 A US 3700305 A
(72) Inventor(s) Alan Lennox Lythgoe Dick van Heijningen	(58) Field of Search UK CL (Edition O) B2E , C7F FPCL FPCX FPDL FPOX FPEL FPEX INT CL ⁶ B44C 1/17 , B44F 1/04 , C03C 17/06 17/09 17/10 17/36 17/38 , C23C 14/06 14/18 , G02B 5/128 ONLINE:WPI,CLAIMS
(74) Agent and/or Address for Service Brookes & Martin High Holborn House, 52-54 High Holborn, LONDON, WC1V 6SE, United Kingdom	

(54) Manufacture of glass microbeads

(57) Glass microbeads having a partial coating of reflective material which comprises embedding or adhering a layer of glass microbeads in or to a coating of a water-susceptible polymer composition on a carrier sheet, applying a reflective coating to the exposed surface of the microbeads and releasing the microbeads from the carrier sheet by washing the polymer composition.

GB 2 316 021 A

MANUFACTURE OF GLASS MICROBEADS

This invention relates to the manufacture of glass microbeads having a partial coating of reflective material.

Glass microbeads have been used for many years for the purpose of gathering incident light and reflecting it back to the viewer. Microbeads of this kind can vary in size from about 10 to 100 microns. In use, they are commonly dispersed in a transparent polymer composition and applied as a coating to produce reflective products such as road signs, car number plates or garments.

It is also known to increase the reflective characteristics of such glass microbeads by coating a part of the surface of the spheres with a reflective material such as a metal coating. This improves the efficiency of the beads in reflecting incident light.

One method of metallising the surface of such microbeads is described in US Patent 3,700,395. According to the method described in this prior patent, glass microbeads are partially embedded in a polythene coating on a paper backing sheet. The exposed area of glass microbeads is then coated with a reflective material such as a transparent material having a different refractive index from the glass of the microbeads. The reflective coated portions of the beads are then coated with polymerisable binder compositions and then laminated to an adhesive-coated cotton cloth. The polyethylene coated paper was then stripped from the beads exposing the glass surface, and leaving the beads embedded in the binder. The beads when embedded in the binder are monodirectional having the metallised surface aligned in the same direction. It is only after the beads have been removed from the support (e.g. by solubilisation

of the binder) that they become random in the sense of the directions in which they reflect light. Since the beads produced in this way will not present an open glass area of the beads to light rays for reflection, their efficiency is considerably less than when the beads are maintained in the same configuration directly from the metallising step.

Also, the process of producing random beads by embedding the beads in molten polyethylene and subsequently removing the beads mechanically, has certain disadvantages. For example, after removing the metallised beads, the paper and the polythene coating cannot be re-used. Secondly, the beads can be damaged in the stripping process.

Also, paper has a moisture content which can affect the level of the vacuum during the metallising step and this leads to irregularities in metallising. The production method described in this prior patent relies on the poor adhesion of glass to the polyethylene, so that any coatings applied to the glass beads to improve the adhesion of the beads in a subsequent processing step causes difficulties in removing the beads from the polythene sheet.

Further, any coatings applied to the glass for the purpose of colouring or manipulating the surface of the glass may adhere better to the polythene than to the glass and would, therefore, be lost in the processing step.

An object of the present invention is therefore to provide a simple and cost-effective method of preparing a mono-layer of glass beads which can be previously treated with a surface material such as a colouring or adhesive promotion material, but without inhibiting the process by which a hemispherical coating of reflective material is applied in a vacuum metalliser or other reflective material coating device.

According to one aspect of the present invention there is provided a method of producing glass microbeads having a partial coating of reflective material, which comprises embedding or adhering a layer of glass microbeads in or to a coating of water-susceptible polymer composition on a carrier sheet, applying a reflective coating to the exposed surface of the microbeads and releasing the microbeads from the carrier sheet by washing the polymer composition.

In accordance with the method of the invention, a layer of microbeads can be deposited with a high degree of precision onto the carrier sheet, which may be a plastic or paper supporting web. The carrier sheet may pick up a mono-layer of beads either when the layer is semi-dry, or when all solvents have been removed.

The diameter of the beads and the thickness and nature of the water-susceptible polymer composition can be selected so that the beads are immersed in the coating on the web to a predetermined extent. In this way, the amount of the microbeads which projects from the surface can be controlled to give the desired amount of reflective area on the exposed surface of the beads. Clearly, this is dependent to some extent on the size of the beads selected. In general, however, the beads can vary from about 10 to 100 microns diameter. Where the beads are intended for use in inks, they will generally have a diameter between about 20 and 40 microns. Beads of larger size, e.g. between 40 and 70 microns, may be used for subsequent distribution over the surface of pre-coated inks and coatings.

The glass of the microbeads can be of any refractive index, e.g. from 1.5 to 3, but generally would be about 1.9. Glasses of high refractive index which

may be used in the present invention are described in US Patents Nos. 3,025,764 and 4,192,576.

The beads may be coated with a reflective material comprising metallic material or may, for example, comprise other reflective material such as glasses of different refractive index, e.g. the reflective material described in US Patent 3,700,305 mentioned above. Normally, the glass will be clear and water-white, but coloured glass beads can be used. The bead may be coloured throughout or be surface-coated with a coloured material.

The method of the invention essentially involves the following steps. Selecting a carrier web, which may comprise a plastic or paper sheet material.

A water susceptible, e.g. water-soluble, polymer composition is applied to the carrier sheet, and the beads are held as a mono-layer on this coated layer with an appropriate area of the bead exposed to receive the vacuum metallised metal film, or other reflective coating. During the passage of the web through a vacuum metalliser, the beads require to be securely held in the polymer layer. This can be achieved by simply coating the web with an appropriate polymer coating and applying the beads from a trough onto the surface of the coating.

The required adhesion may be achieved by depositing the beads on the coating while it is (a) still wet, (b) when partially dry or, (c) fully dry. In the case of (c), the coating requires to be tacky before applying the beads.

In the case of procedure (a), the degree of wetting of the beads is determined by (1) the viscosity of the liquid, (2) the type of solvent used and its wetting power, (3) the thickness of the layer, (4) the diameter of the beads and, (5) the surface tension characteristics of the beads.

In the case of a partially dried layer, the same considerations apply and the viscosity will need to be very much higher so that the tendency of the beads to be swallowed up and fully immersed will be reduced.

The formulation of the coating will, however, be of greater importance in so far as the softness and receptivity of the coating becomes more important. If the coating is too soft, the bead may be buried and this may also be true if the layer is too thick. The beads may require pressure applied to force them into a dried or semi-dried layer. This can be achieved using a roller or calendering operation.

In the case of the fully dried layer, the formulation is extremely important since the layer requires to have the correct level of softness, combined with sufficient tack so that the beads are bonded to the layer with the beads retained at the correct depth.

Preferably, the binder layer is water-soluble, so that after the beads have been metallised or other reflective coating applied, they can be easily and cheaply removed from the web by mere washing with water.

Water is a very poor wetting solvent for plastic surfaces and it is, therefore, preferred that binder compositions are selected, which are both organic solvent soluble, as well as susceptible to water. Preferably, the binder should be soluble, both in an organic solvent which is capable of wetting the surface of the carrier web, while retaining ready solubility in water after drying.

The binder should also be capable of being tackified to exactly the right degree of tack so that the mono-layer of beads is held securely to the surface of the web at the correct depth of penetration into the layer. Care should also be taken that when using water-soluble plasticisers to tackify the binder layer, they

should not swamp the beads and prevent them being coated with the metallising layer.

Particularly useful polymers for the purposes of the present invention include cellulosic polymers such as polyvinyl pyrrolidone, hydroxypropylcellulose, vinyl methyl ethers polymers, such as Iutanol M40 from BASF, or copolymers of methylvinylether with a polymerisable anhydride such as maleic anhydride or ethylene maleic anhydride. These polymers are soluble both in organic solvents such as alcohols or ketones, e.g. isopropyl alcohol or acetone to yield smooth clear coatings. They are also compatible with water-soluble and non-volatile materials such as glycerol which can, therefore, be used as a plasticising tackifier.

Coatings of such polymers can also be used without a tackifier, provided that the microbeads are applied while the coating is still wet or semi-dried. However, when a dry film is required to be used, layers can be post-tackified with the water-soluble plasticiser. Vinyl methyl ethers are very tacky when dried and normally require no additional tackifier. They are modified with other water-soluble polymers, such as hydroxy alkyl celluloses, e.g. hydroxy propyl cellulose, e.g., Klucel from Hercules.

Coatings of the kind described above remain soluble in water, so that after the mono-layer of beads has been applied and the beads metallised in a vacuum metalliser, the beads can be separated from the web by washing off with water. The beads can also be removed from the web by scraping the adhesive and beads off the carrier web with a knife. The beads can then be more easily washed and separated from the adhesive.

This is a cheap and effective way of producing hemispherically metallised beads, which can then be easily collected and dried. Moreover, the plastic carrier web can be re-used in the process.

The following example is given to illustrate the present invention.

EXAMPLE 1

A web of 25 micron thick polypropylene sheet material was coated with a binder composition comprising:

25 parts of methylvinyl maleic anhydride copolymer

10 parts of glycerol

60 parts of isopropyl alcohol, and

5 parts of ethyl glycol.

The above parts were all by weight.

The resulting composition was a clear solution and was coated onto the carrier web using a doctor blade to provide a dry coated thickness of about 40 microns.

The resulting layer was tacky and was coated by cascading glass beads having a diameter of about 40 to 60 microns over the surface of the coating, and the excess beads shaken off.

The resulting assembly was passed between lip rollers to press the beads to the correct depth into the binder coating, following which the web was passed through a vacuum metalliser to coat the exposed portions of the beads with an aluminium layer.

After the metallising treatment, the web was passed through a water spray wash to remove the beads which were then filtered and dried.

The resulting random metallised beads so produced were free flowing and could be dusted on the surface of tacky liquids or solids to give mono-layers of reflective beads. The resulting layers were highly reflective and could be used for fabrics for night safety or on the sides of vehicles or bicycles or road signs.

EXAMPLE 2

Example 1 was repeated except that a web of 20 micron thick polyester film was used as the carrier web and this was coated with a binder composition consisting of:

- 10-40 parts hydroxy propyl cellulose
- 5-20 parts trimethylol propane
- 40-85 parts isopropyl alcohol

The above parts were all by weight.

The binder composition was applied to the web to give a dry coating thickness of 20 - 50 microns.

Glass beads of refractive index between 1.5 to 2.7 and of diameter between 30 - 80 microns were spread on the coating either when partially or fully dried such that 40 to 60% of the surface of the beads was exposed.

The web was then passed through a vacuum metalliser to coat the exposed area of beads with aluminium or other reflective material which gives a specularly reflective surface such as silver, gold or cryolite.

The beads were then washed off the web with water, strained and dried.

EXAMPLE 3

Example 2 was repeated except that instead of having a vacuum metallised layer over the beads, the reflective layer is provided by spraying the

beads with a leafing aluminium dispersed in a non water soluble vehicle such as nitrocellulose.

CLAIMS:-

1. A method of producing glass microbeads having a partial coating of reflective material which comprises embedding or adhering a layer of glass microbeads in or to a coating of a water-susceptible polymer composition on a carrier sheet, applying a reflective coating to the exposed surface of the microbeads and releasing the microbeads from the carrier sheet by washing the polymer composition.
2. A method as claimed in claim 1 wherein the polymer composition is water-soluble.
3. A method as claimed in claim 2, wherein the polymer comprises a vinyl methyl ether.
4. A method as claimed in claim 2 or 3 wherein the polymer composition comprises a polymer of an unsaturated acid or anhydride.
5. A method as claimed in any one of claims 2 to 4, wherein the polymer composition comprises a copolymer of an unsaturated monomer and an unsaturated anhydride.
6. A method as claimed in any one of the preceding claims wherein the polymer composition includes a water-soluble tackifier.
7. A method as claimed in any one of the preceding claims wherein the reflective coating is a metallised coating.
8. Glass microbeads having a partial coating of reflective material whenever produced by the method claimed in any one of the preceding claims.



The
Patent
Office

II

Application No: GB 9716893.4
Claims searched: 1 to 8

Examiner: R.J.MIRAMS
Date of search: 10 November 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): B2E, C7F (FPCL, FPCX, FPDL, FPDX, FPEL, FPEX).

Int Cl (Ed.6): B44C 1/17. B44F 1/04. C03C 17/06, 17/09, 17/10, 17/36, 17/38. C23C 14/06, 14/18. G02B 5/128.

Other: ONLINE: WPI, CLAIMS.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	US3971692A (Anderson)	
A	US3700305A (Bingham)	

X Document indicating lack of novelty or inventive step	A Document indicating technological background and/or state of the art.
Y Document indicating lack of inventive step if combined with one or more other documents of same category.	P Document published on or after the declared priority date but before the filing date of this invention.
& Member of the same patent family	E Patent document published on or after, but with priority date earlier than, the filing date of this application.